

Theoretical study of molecular electronic excitations and optical transitions of C_{60}

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We report results on *ab initio* calculations of excited states of the fullerene molecule by using configuration interaction (CI) approach with singly excited determinants (SCI). We have used both the experimental geometry and the one optimized by the density functional method and worked with basis sets at the cc-pVTZ and aug-cc-pVTZ level. Contrary to the early SCI semiempirical calculations, we find that two lowest ${}^1T_{1u} \leftarrow {}^1A_g$ electron optical lines are situated at relatively high energies of ~ 5.8 eV (214 nm) and ~ 6.3 eV (197 nm). These two lines originate from two ${}^1T_{1u} \leftarrow {}^1A_g$ transitions: from HOMO to (LUMO+1) ($6h_u \rightarrow 3t_{1g}$) and from (HOMO-1) to LUMO ($10h_g \rightarrow 7t_{1u}$). The lowest molecular excitation, which is the ${}^1{}^3T_{2g}$ level, is found at ~ 2.5 eV. Inclusion of doubly excited determinants (SDCI) leads only to minor corrections to this picture. We discuss possible assignment of absorption bands at energies smaller than 5.8 eV (or λ larger than 214 nm).

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I. INTRODUCTION

The buckminsterfullerene molecule C_{60} attracts much attention of theoreticians since its discovery in 1985 [1, 2]. Indeed, the role of the fullerene molecule in quantum chemistry is unique because of its highest group (I_h) of symmetry leading to a high degeneracy of molecular orbitals (MOs). The MOs of C_{60} are classified according to irreducible representations (irreps) of I_h , which are a , t_1 , t_2 , g , and h . (The dimensions of the irreps are 1, 3, 3, 4, and 5, correspondingly.) For example, the highest occupied molecular orbital (HOMO) is a fivefold electron shell of h_u symmetry while the lowest unoccupied molecular orbital (LUMO) is a threefold level of t_{1u} symmetry.

High degeneracies of molecular orbitals imply a complex electronic structure [3, 4, 5, 6]. However, since all electron shells of the neutral C_{60} molecule are completely filled, the ground state is of 1A_g symmetry and the many-electron states of the molecule are not revealed. The situation changes when the fullerene molecule is excited. Then a few electrons of C_{60} are promoted to a higher energy, and some of electron shells become open. The electrons of the open shells exhibit correlated behavior and form many electron levels called molecular terms [2, 7, 8, 9, 10], which are also classified according to the irreducible representations of the icosahedral symmetry (A , T_1 , T_2 , G , and H). Thus, a careful study of these correlations is needed for calculations of optical transitions [11, 12] and molecular excitations. It is worth mentioning that intramolecular correlations play an important role in alkali doped fullerenes, leading to superconductivity, magnetic behavior and metal-insulator transitions

TABLE I: Selected molecular excitations calculated with semiempirical CI calculations and in the present work. Energies are in eV. N_{CSF} stands for the number of configuration state functions used for CI.

Ref. method N_{CSF}	[9] PPP 134	[8] QCFF/ π 266	[10] CNDO/S 900	this work <i>ab initio</i> SCI 2857
	planar	3D		
${}^1{}^3T_{2g}$	2.456	2.232	2.06	2.549
${}^1{}^1G_u$	3.603	3.381	3.21	4.700
${}^1{}^1H_u$	3.635	3.391	3.15	4.771
${}^1{}^1T_{1u}$	4.227	4.000	4.08	3.40 5.796
$2{}^1T_{1u}$	4.750	4.681	4.53	4.06 6.335

[2, 13, 14].

Computations of many electron states of C_{60} is a challenge for the modern quantum theory [15]. In the literature there are few works devoted to the problem of calculations of molecular excitations of the fullerene [7, 8, 9, 10], but to the best of our knowledge all of them are semiempirical and are based only on singly excited configuration interaction (CI). We reproduce some of their computed levels in Table I. The calculation of Negri *et al.*, Ref. [8], employed a semiempirical (QCFF/ π) method, and took into account 196 configuration state functions (CSF). The first excited state (${}^1{}^3T_{2g}$) was found at 2.06 eV, while ${}^1{}^1T_{1u}$ and $2{}^1T_{1u}$ levels at 4.08 and 4.53 eV. A PPP-CI (Pariser-Parr-Pople Configuration Interaction) calculation which includes 134 CSF finds first two ${}^1T_{1u}$ levels at 4.00 eV, 4.68 eV and 6.69 eV, with the first excited ${}^3T_{2g}$ level at 2.23 eV. Finally, CNDO/S calculations of Braga *et al.* based on 808 and 900 configurations predicts that ${}^1{}^1T_{1u}$ is lowered to 3.4 eV, while the three most intense transitions are at 4.38, 5.24 and 5.78 eV. Unfortunately, all of the CI calculations reported in Refs. [7, 8, 9, 10] are crucially dependent on a number of approximations for matrix elements and therefore cannot be considered as a true *ab initio* approach.

In the present study in comparison with Refs. [7, 8, 9,

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10] we employ the *ab initio* treatment, which represents a new level of CI calculations of the fullerene molecule.

II. METHOD OF CALCULATION

A. Configuration Interaction

A well known recipe for correlations is the method of configuration interaction (CI) [15]. The basic idea is to diagonalize the N -electron Hamiltonian in a basis of N -electron functions (Slater determinants). In principle, the full CI method with infinite number of the molecular orbitals provides an exact solution of the many-electron problem. In practice, even for small molecules and moderately sized one-electron basis sets, the number of N -electron determinants is enormous. To avoid it, we first introduce an active space which comprises a set of highest occupied molecular orbitals (HOMOs) and a set of lowest unoccupied molecular orbitals (LUMOs). The space of the MOs is divided into three subspaces: the inactive, the active and the external orbitals. The inactive orbitals are double occupied, while the external orbitals are unoccupied. Within the chosen active space one can consider various approximations to the complete active space CI matrix by truncating the many-electron trial function at some excitation level. For example, singly excited CI (SCI) approach has been proven to be adequate as a first approximation for the neutral molecule because all electron shells of C_{60} are filled up. In the following for large active spaces (AS) we use SCI, but also consider singly and doubly excited determinants (SDCI) for smaller AS, and a complete active space (CAS) CI method [16] for important active spaces of two molecular shells (8 MOs). The computer code for the CI calculations is the modified and extended version of the earlier program, Ref. [5].

B. Computational details

The CI calculations have been carried out with the set of molecular orbitals (MOs) obtained from the restricted Hartree-Fock (RHF) self-consistent-field calculation [15] of the neutral fullerene molecule. In the following we have used two sets of coordinates of the C_{60} molecule. First set was obtained in Ref. [17] (DFT/B3LYP method). Two different C-C bond lengths were $R_5 = 1.4507 \text{ \AA}$ (C-C bond in pentagons) and $R_6 = 1.3906 \text{ \AA}$ (short C-C bond in hexagons). The second set corresponds to the experimental geometry [18] with $R_5 = 1.448 \text{ \AA}$ and $R_6 = 1.404 \text{ \AA}$.

We have used our original RHF computer program [19], which uses the resolution of the identity [20] (RI) method for calculation of the two-electron Coulomb integrals. The series of the RI (auxiliary) basis sets, HCNO. x , were designed for the RI-convergent calculations the RHF total energies and the electronic properties of molecules

TABLE II: Electron shells of C_{60} . E_{MO} is the one-electron Hartree-Fock MO energy (in eV). The basis set is aug-cc-pVTZ(-f). $E_{tot} = -61832.163 \text{ a.u.}$

	MOs	symmetry	E_{MO}
LUMO+18	244-248	$8h_u$	4.303
LUMO+17	239-243	$14h_g$	3.855
LUMO+16	235-238	$8g_g$	3.794
LUMO+15	232-234	$10t_{2u}$	3.300
LUMO+14	229-231	$4t_{1g}$	3.280
LUMO+13	228	$6a_g$	3.161
LUMO+12	225-227	$8t_{1u}$	3.115
LUMO+11	220-224	$7h_u$	2.557
LUMO+10	215-219	$13h_g$	2.418
LUMO+9	211-214	$7g_g$	2.254
LUMO+8	206-210	$12h_g$	2.121
LUMO+7	203-205	$9t_{2u}$	1.994
LUMO+6	200-202	$8t_{2u}$	1.774
LUMO+5	196-199	$7g_u$	1.751
LUMO+4	195	$5a_g$	1.496
LUMO+3	190-194	$11h_g$	1.398
LUMO+2	187-189	$7t_{2u}$	1.150
LUMO+1	184-186	$3t_{1g}$	0.947
LUMO	181-183	$7t_{1u}$	-0.817
HOMO	176-180	$6h_u$	-7.834
HOMO-1	171-175	$10h_g$	-9.627
HOMO-2	167-170	$6g_g$	-9.890
HOMO-3	163-166	$6g_u$	-12.589
HOMO-4	160-162	$6t_{2u}$	-13.050

containing hydrogen, carbon, nitrogen and oxygen elements as discussed in [19]. Here x indicates (but not exactly equal to) the accuracy (in atomic units) of the total RHF energy: smaller x implies more RI functions and more accurate RI basis set. The accuracy of the RI basis set is almost independent of the choice of molecular basis set. Having performed test calculations with Pople's 6-31G* MO basis set [21, 22] and the HCNO. x RI series we have found out that a reasonable convergence is achieved for the HCNO.001 RI basis set, which is used for all further calculations.

Throughout the paper we have adopted short notation aug-cc-pVTZ(-f) for Dunning's augmented correlation consistent polarizable valence triple zeta molecular basis set aug-cc-pVTZ [22, 23] where all polarization functions of f -symmetry are excluded from the set.

III. RESULTS AND DISCUSSION

A. SCI excitation spectrum of C_{60}

The main results are shown in Tables II and III. The (HOMO-4) to (LUMO+18) energies of C_{60} calculated with the aug-cc-pVTZ(-f) basis set are quoted in Table II. We then define a broad active space spanned by these MOs and occupied with 42 correlated electrons and use it in our SCI calculations. Table III displays the resulting spectrum of lowest molecular excitations. In order to evaluate the influence of two bond lengths of the fullerene

TABLE III: Lowest excitations of C_{60} . OG refers to the bond lengths of C_{60} optimized by DFT, Ref. 17, EG to the experimental ones, Ref. 18.

	${}^3T_{2g}$	${}^3T_{1g}$	${}^1T_{2g}$	3H_g	${}^1T_{1g}$	3G_g	1G_g	3G_u
OG	2.549	3.041	3.229	3.287	3.416	3.417	3.538	3.595
EG	2.384	2.877	3.051	3.100	3.239	3.235	3.357	3.464
	${}^3T_{1u}$	${}^3T_{2u}$	1H_g	3H_u	${}^1T_{2u}$	1G_u	1H_u	${}^3T_{2u}$
OG	3.917	3.996	4.079	4.304	4.611	4.700	4.771	4.960
EG	3.771	3.801	3.906	4.154	4.447	4.534	4.588	4.822
	3G_u	1G_u	3G_g	3H_u	1H_u	3H_u	${}^1T_{1u}$	${}^3T_{1u}$
OG	5.163	5.291	5.355	5.454	5.598	5.732	5.796	5.972
EG	5.023	5.157	5.300	5.295	5.445	5.662	5.667	5.849
	3H_u	${}^1T_{2u}$	3G_u	${}^3T_{2g}$	1H_u	1G_u	3H_u	1H_u
OG	5.986	6.001	6.019	6.124	6.141	6.208	6.236	6.264
EG	5.823	5.872	5.873	6.041	5.954	6.021	6.188	6.218
	${}^1T_{1u}$	3G_u	${}^3T_{1u}$	1H_g	${}^3T_{2u}$	${}^1T_{2g}$	3H_u	3H_g
OG	6.335	6.337	6.340	6.412	6.422	6.444	6.501	6.518
EG	6.182	6.216	6.206	6.340	6.275	6.360	6.395	6.400

molecule, we have performed calculations with two different geometries of C_{60} : optimized by DFT [17] and the experimental one [18]. Inspection of Table III shows that the order of levels is mainly conserved, while a typical numerical deviation is ~ 0.2 eV. From this we conclude that a possible small change of the C_{60} bond lengths do not change appreciably its excitation spectrum.

The most striking feature of the calculation is the relatively high energy position of the two lowest ${}^1T_{1u}$ excitations (given already in Table I) with oscillator strengths 1.02 and 0.16, respectively. For a review on oscillator strengths in semiempirical calculations see Ref. [24]. In the following we limit ourselves to the optimized geometry [17] and consider mainly the problem of convergency and adequacy of the SCI calculation leaving discussion and conclusions until Sec. IV.

B. Basis set dependence

To study basis set dependence of the SCI excitation spectrum we narrowed active space to 167–219 MOs, see Table II. This active space consists of 14 electron shells (from HOMO-2 to LUMO+10) filled by 28 correlated electrons. Such calculations require less computer time in comparison with the calculation with the active space of Table II reported in Table III, but lead to a less accurate molecular excitation spectrum.

The results of such SCI calculations are presented in Table IV. Notice that the order of the levels is almost the same for the group of 6-31G*, cc-pVDZ, cc-pVTZ and cc-pVTZ(-f) basis sets. The deviations of the molecular excitation energies are rather small, of the order of 0.1 eV. The molecular energies are close to a convergence and the basis f-functions have a small effect on calculated values. On the other hand the inclusion of diffuse functions of aug-cc-pVDZ(-f) and aug-cc-pVTZ(-f) leads to a rearrangement of electronic levels, Table IV, which indicates that aug-cc-pVTZ(-f) is the best set for SCI

TABLE IV: Energy spectrum of C_{60} with various basis sets. Basis sets are cc-pVDZ [DZ], aug-cc-pVDZ [aDZ], cc-pVTZ [TZ], cc-pVTZ without the f -functions [TZ(-f)], and aug-cc-pVTZ(-f) [aTZ(-f)], see text for details.

Γ	6-31G*	DZ	TZ	TZ(-f)	Γ	aDZ	Γ	aTZ(-f)
${}^3T_{2g}$	2.593	2.575	2.582	2.573	${}^3T_{2g}$	2.900	${}^3T_{2g}$	2.669
${}^3T_{1g}$	3.114	3.071	3.053	3.048	${}^3T_{1g}$	3.261	${}^3T_{1g}$	3.107
${}^1T_{2g}$	3.322	3.276	3.249	3.248	${}^1T_{2g}$	3.325	${}^1T_{2g}$	3.254
3H_g	3.384	3.336	3.312	3.308	3H_g	3.474	3H_g	3.390
${}^1T_{1g}$	3.522	3.467	3.434	3.432	${}^1T_{1g}$	3.541	${}^1T_{1g}$	3.439
3G_g	3.540	3.481	3.447	3.445	3G_g	3.547	3G_g	3.477
1G_g	3.654	3.594	3.558	3.556	1G_g	3.649	1G_g	3.578
3G_u	3.672	3.675	3.700	3.685	${}^3T_{1u}$	4.154	3G_u	3.995
${}^3T_{1u}$	3.899	3.884	3.884	3.875	${}^3T_{2u}$	4.196	${}^3T_{1u}$	4.069
${}^3T_{2u}$	4.002	3.993	3.995	3.987	1H_g	4.288	${}^3T_{2u}$	4.132
1H_g	4.231	4.159	4.112	4.111	3G_u	4.355	1H_g	4.136
3H_u	4.383	4.365	4.365	4.356	3H_u	4.754	3H_u	4.541
${}^1T_{2u}$	4.650	4.632	4.625	4.618	${}^1T_{2u}$	4.889	${}^1T_{2u}$	4.751
1G_u	4.831	4.802	4.779	4.777	1G_u	4.897	1G_u	4.849
1H_u	4.862	4.835	4.816	4.811	1H_u	4.976	1H_u	4.899
${}^3T_{2u}$	5.120	5.075	5.053	5.045	${}^3T_{2u}$	5.500	${}^3T_{2u}$	5.241
3G_u	5.402	5.337	5.293	5.289	3G_u	5.651	3G_u	5.350
3G_g	5.443	5.398	5.392	5.373	1G_u	5.771	1G_u	5.451
1G_u	5.514	5.448	5.404	5.400	3H_u	5.603	3H_u	5.529
3H_u	5.576	5.524	5.490	5.486	1H_u	5.722	1H_u	5.652
1H_u	5.764	5.704	5.661	5.659	${}^1T_{1u}$	6.116	${}^1T_{1u}$	5.880
${}^1T_{1u}$	5.873	5.826	5.793	5.785	3H_u	6.221	3G_g	5.919
3H_u	5.940	5.859	5.810	5.797	${}^1T_{2u}$	6.236	${}^1T_{2u}$	6.071
${}^3T_{1u}$	6.057	5.992	5.946	5.937	3G_g	6.249	3H_u	6.075
3H_u	6.087	6.032	5.993	5.987	${}^3T_{1u}$	6.280	${}^3T_{1u}$	6.092
3G_u	6.116	6.067	6.030	6.022	1H_u	6.254	3H_g	6.098
${}^1T_{2u}$	6.165	6.096	6.048	6.046	1G_u	6.281	3G_u	6.103
${}^3T_{2g}$	6.194	6.113	6.054	6.042	${}^3T_{2g}$	6.543	1H_u	6.198
1H_u	6.299	6.246	6.202	6.199	${}^1T_{1u}$	6.577	1G_u	6.264
1G_u	6.363	6.314	6.274	6.271	3G_u	6.954	${}^3T_{2g}$	6.325
3G_u	6.445	6.386	6.346	6.340	3H_g	6.960	${}^1T_{1u}$	6.371
${}^3T_{1u}$	6.457	6.402	6.360	6.356	${}^3T_{1u}$	7.118	${}^3T_{1u}$	6.413
${}^1T_{1u}$	6.462	6.407	6.365	6.362	${}^1T_{1u}$	7.122	3G_u	6.452

calculations.

C. Active space dependence

Here we study the dependence of SCI excitation energies on the choice of active space. In Table V we keep the lower boundary active shell, which is the HOMO-4 ($6t_{2u}$) level unchanged and systematically increase the upper electron boundary. Inspection of Table V shows that we are close to a convergence for the broad active space of 160–248 MOs, shown in Table II. Therefore, we do not expect drastic changes if the active space is increased even further. Notice however, that the optically active ${}^1{}^1T_{1u}$ and ${}^2{}^1T_{1u}$ levels monotonically decrease with the increase of active space.

TABLE V: Dependence of selected energy levels on chosen active space. The active space consists of the MOs between lower and upper MOs. The lower MO is 160, which corresponds to the HOMO-4 ($6t_{2u}$) level. The upper MO changes from LUMO+1 to LUMO+18. The basis set is aug-cc-pVTZ(-f).

upper MO	186	189	194	199	202	205	210	214
1^3T_{2g}	2.889	2.889	2.889	2.889	2.887	2.833	2.713	2.712
1^1G_u	4.808	4.808	4.808	4.808	4.807	4.801	4.758	4.758
1^1H_u	4.898	4.898	4.898	4.898	4.898	4.891	4.836	4.836
1^1T_{1u}	6.230	6.230	6.230	6.230	6.230	6.212	6.028	6.026
2^1T_{1u}	7.210	7.210	7.194	7.172	7.112	6.936	6.421	6.419
upper MO	219	224	227	231	234	238	243	248
1^3T_{2g}	2.633	2.633	2.623	2.618	2.600	2.599	2.584	2.549
1^1G_u	4.730	4.730	4.727	4.721	4.719	4.719	4.715	4.700
1^1H_u	4.802	4.802	4.798	4.793	4.791	4.790	4.785	4.771
1^1T_{1u}	5.862	5.862	5.862	5.860	5.839	5.838	5.816	5.796
2^1T_{1u}	6.354	6.354	6.352	6.352	6.348	6.348	6.343	6.335

D. Beyond SCI approximation for small AS

We recall that all the results reported earlier have been obtained under approximation that only singly excited configurations (SCI) are taken into account. It is therefore instructive to estimate the accuracy of this assumption. Since the active space shown in Table II is very big, we study this problem by considering fewer active MOs. We limit ourselves to four most important active spaces: HOMO+LUMO ($6h_u + 7t_{1u}$), HOMO+(LUMO+1) ($6h_u + 3t_{1g}$), (HOMO-1)+LUMO ($10h_g + 7t_{1u}$), and (HOMO-1)+(LUMO+1) ($10h_g + 3t_{1g}$). All of them consists of 8 active MOs (five from h and three from t_1), which accommodate 10 correlated electrons. For each of the active spaces we have performed four calculations: SCI, singly and double excited CI (SD-CI), singly, doubly and triply excited CI (SDT-CI), and with all possible excitations. The latter is so called complete active space (CAS-CI) calculation [16]. In Tables VI-IX we give the results for the four cases, respectively. Notice that the CAS-CI results are very close to that of SDT-CI, while both SCI and SDCI molecular energies miss the precise values by a typical error of ~ 0.1 eV. Furthermore, as a rule SDCI energies overestimate the real values. It is very probable that the same conclusions are applicable to a calculation with a large AS. Indeed, our SDCI calculations [25] with a large AS of 186-248 MOs unambiguously indicate an increase of 1^1T_{1u} energies in comparison with the SCI values: the energy of the first transition changes from 5.997 to 6.291 eV, while the energy of the second from 6.395 to 7.154 eV. Thus the SDCI results underline the importance of SDT-CI calculation for the C_{60} molecule.

It is worth noting that two lowest $1^1T_{1u} \leftarrow 1^1A_g$ transitions can be found already in Tables VII and VIII. Their energies are quite high, 6.44 eV ($6h_u \rightarrow 3t_{1g}$) and 6.96 eV ($10h_g \rightarrow 7t_{1u}$). If both of the 1^1T_{1g} levels are included in a CI calculation, they interact with each other, because

TABLE VI: Lowest excitations of C_{60} , calculated with 10 correlated electrons in the $6h_u + 7t_{1u}$ limited active space (see text for details).

excitation level	S	SD	SDT	all (CAS)
1^1A_g	0	0	0	0
3^3T_{2g}	3.312	3.383	3.338	3.338
3^3T_{1g}	3.482	3.551	3.511	3.511
1^1T_{2g}	3.590	3.661	3.622	3.623
3^3H_g	3.640	3.699	3.651	3.651
1^1T_{1g}	3.691	3.761	3.713	3.713
3^3G_g	3.709	3.768	3.726	3.726
1^1G_g	3.769	3.833	3.791	3.791
1^1H_g	4.298	4.337	4.281	4.280

TABLE VII: Lowest excitations of C_{60} , calculated with 10 correlated electrons in the $6h_u + 3t_{1g}$ limited active space (see text for details).

excitation level	S	SD	SDT	all (CAS)
1^1A_g	0	0	0	0
3^3T_{2u}	5.188	5.322	5.239	5.239
3^3T_{1u}	5.234	5.368	5.297	5.298
3^3G_u	5.410	5.544	5.470	5.471
3^3H_u	5.461	5.595	5.529	5.530
1^1H_u	5.550	5.684	5.616	5.617
1^1G_u	5.594	5.728	5.661	5.662
1^1T_{2u}	5.692	5.826	5.760	5.761
1^1T_{1u}	6.443	6.577	6.438	6.439

TABLE VIII: Lowest excitations of C_{60} , calculated with 10 correlated electrons in the $10h_g + 7t_{1u}$ limited active space (see text for details).

excitation level	S	SD	SDT	all (CAS)
1^1A_g	0	0	0	0
3^3G_u	5.218	5.497	5.331	5.334
3^3T_{1u}	5.233	5.512	5.371	5.374
3^3T_{2u}	5.440	5.719	5.562	5.565
3^3H_u	5.457	5.737	5.596	5.600
1^1T_{2u}	5.548	5.828	5.679	5.682
1^1G_u	5.580	5.860	5.716	5.720
1^1H_u	5.605	5.884	5.737	5.741
1^1T_{1u}	6.997	7.277	6.959	6.960

TABLE IX: Lowest excitations of C_{60} , calculated with 10 correlated electrons in the $10h_g + 3t_{1g}$ limited active space (see text for details).

excitation level	S	SD	SDT	all (CAS)
1^1A_g	0	0	0	0
3^3H_g	7.072	7.110	7.075	7.075
3^3T_{2g}	7.116	7.154	7.125	7.125
3^3G_g	7.174	7.224	7.194	7.194
3^3T_{1g}	7.192	7.236	7.209	7.209
1^1T_{2g}	7.299	7.348	7.320	7.320
1^1T_{1g}	7.337	7.383	7.353	7.353
1^1G_g	7.388	7.442	7.415	7.415
1^1H_g	7.868	7.898	7.859	7.859

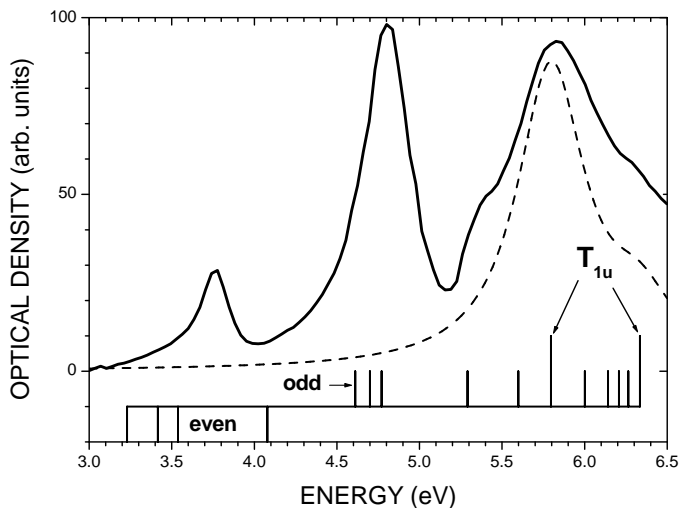


FIG. 1: Comparison between the experiment data on optical density, Ref. 11, and the calculated spin singlet lines of C_{60} . The dashed line is the contribution from two T_{1u} transitions broadened with the line width of 0.5 eV. The MO basis set is aug-cc-pVTZ(-f), the bond lengths are taken from Ref. 17.

they are of the same symmetry. Nevertheless, the lowest 1^1T_{1u} level stays predominantly of the $6h_u \rightarrow 3t_{1g}$ origin, while the 2^1T_{1u} level is mainly of the $10h_g \rightarrow 7t_{1u}$ character. Notice that the lowest part of molecular excitations of C_{60} stems from the HOMO+LUMO ($6h_u+7t_{1u}$) active space, Table VI.

IV. DISCUSSION AND CONCLUSIONS

We have found that the lowest electron optical transitions are at ~ 5.8 eV (214 nm) and ~ 6.3 eV (197 nm), which are at disagreement with the results obtained with the early semiempirical CI calculations [8, 9, 10]. We have analyzed the influence on the SCI excitation spectrum from the approximations used in our calculation and concluded that all of them are unlikely to change the computed values substantially. Thus, according to our calculations, the first allowed optical transition of C_{60} lies very close to the characteristic interstellar absorption at 217 nm [1, 26].

From the *ab initio* study we come to the conclusion that early semiempirical configuration interactions of the fullerene molecule, Refs. [8, 9, 10] result in systematically smaller excitation energies, see Table I. This was also the case for the molecular ion C_{60}^{2-} , for which the $1A_g$ spin singlet ground state was obtained [27]. As shown in Refs. [5, 6] the ground state is rather the $3T_{1g}$ spin triplet in accordance with Hund's rules.

Calculated oscillator strengths of two lowest optical transitions to 1^1T_{1u} and 2^1T_{1u} states in the largest AS (Table II) are 1.02 and 0.16, respectively. QCFF/ π method employed by Negri *et al.* [8] resulted in 0.61

and 0.41 for oscillator strengths of two lowest transitions while Braga *et al.* [10] [CNDO/S method] obtained 0.08 and 0.41. As we remarked before our *ab initio* energies of two lowest 1^1T_{1u} transitions are very different from the semiempirical ones and a direct comparison of the oscillator strengths is probably premature. On the other hand, early semiempirical calculations give only a vague correspondence with the experimental optical density [11], see Fig. 14 of Ref. [24]. In order to achieve a good comparison Westin *et al.* used a screened response oscillator strength distribution calculated with an adjustable parameter ν [24]. Under such conditions the theoretical curve reproduces the three experimental bands shown in Fig. 1. Our present *ab initio* study accounts only for the 6 eV band, Fig. 1. Thus, two other bands are probably of the electron-vibronic origin [28]. The situation is not uncommon for complex molecules and it occurs for example at the $1B_{2u} \leftarrow 1A_{1g}$ (3200 Å) transition of naphthalene as discussed in Chapter II γ of Ref. [28].

The optical spectrum of C_{60} also shows some similarities with that of benzene [28, 29]. Lowest excited states of benzene are spin triplets, while the first electronically allowed optical transition ($1^1E_{1u} \leftarrow 1A_{1g}$) is situated at relatively high energy of ~ 7 eV [29, 30]. In benzene two lowest absorption bands at 4.90 and 6.20 eV were unambiguously assigned to the excited states of 1^1B_{2u} and 1^1B_{1u} , respectively [29, 30]. These bands are electronically forbidden and occur only due to the electron-vibronic coupling, which underlines the importance of the Herzberg-Teller mechanism [28] for the molecule. It is plausible that the same scenario applies to the C_{60} fullerene, and optical lines at smaller energies are caused by vibronic coupling to numerous electron states in these energy regions, Fig. 1. Indeed, there are indications that optical bands observed in the low region of the absorption spectrum of C_{60} can be interpreted as false origins of states of the T_{1g} symmetry [31]. It is worth noting that singlet and triplet states of C_{60} can be distinguished by low energy electron spectroscopy [32].

Unfortunately, the electronic spectrum of C_{60} is not so well understood as benzene's, which has a long history of calculations and interpretations [28, 29]. Although in all our SCI and SD-CI calculations the 1^1T_{1u} level remains at high energy of ~ 6 eV, we think that there is still a possibility for it to be lowered if a calculation with a higher level of excitations within the CI approach is performed (at least SDT-CI). Interestingly, this is the case for the first allowed optical transition ($1^1E_{1u} \leftarrow 1A_{1g}$) in benzene. The CASSCF calculation of C_6H_6 (6 π electrons distributed among 12 π MOs) places the 1^1E_{1u} level at a high energy of 8.77 eV, while a multireference Møller-Plesset perturbation theory (MRMP) on the CASSCF states lowers this energy by 1.84 eV to 6.93 eV (Table 2 of Ref. [29]). The last value is in perfect agreement with the experiment (6.94 eV, Ref. [30]). Notice that MRMP is known for effectively accounting for high excitations.

In conclusion, our S-CI and SD-CI calculations indicate that the first electronically allowed transition

$1^1T_{1u} \leftarrow 1A_{1g}$ is located at a relatively high energy of 5.8–6.0 eV. Our finding opens up a very interesting question on assignment of two lowest absorption bands at 3.8 and 4.8 eV found experimentally [11, 12]. There are two ways to reconcile our calculations with the experiment. First, the 1^1T_{1u} excited state can be lowered at the level of

SDT-CI or more refined CI calculations. The second scenario is the electron-vibronic coupling (Herzberg-Teller mechanism) [28], which is the case for benzene. Further investigations and *ab initio* calculations are needed to clarify this issue.

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